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HOSOYA INDEX OF SOME POLYMERS

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An explicit expression for the Hosoya index (Z) of a class of polymers is obtained. Its special cases reduce to a few previously known formulas for Z. The Z-value of the polymer is a function of the Z of the monomer unit and some of its fragments as well as of the number of monomer units (n). It is an exponential function of n. A fully analogous combinatorial reasoning leads to formulas for the number of Kekulé structures, matching polynomial and characteristic polynomial of the same class of polymers.

INTRODUCTION

There is nowadays an extensive literature available on the topological index of Hosoya [1] (Z) and its applications to various problems of physical chemistry [2], thermodynamics [3] and statistical physics [4]. Quite recently novel bounds [5] and approximate formulas [6-8] for Z were deduced.

The Hosoya index of a graph G with m edges is given by

$$Z = Z(G) = \sum_{k=0}^{m} m(G, k)$$

where m(G, k) is the number of k-matchings of G i.e. the number of selections of k mutually non-touching edges in G. By definition, m(G, 0) = 1 and m(G, 1) = m.

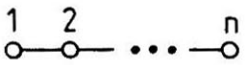
The calculation of Z is quite cumbersome, especially for large polycyclic molecules. Therefore it would be useful to know explicit combinatorial expressions for the Hosoya index of homologous series of molecules. The first such formula, reproducing the Z-value of the normal alkane with n carbon atoms, was reported in Hosoya's first publication [9]:

$$Z(P_n) = 20^{-1/2}\, 2^{-n}[(1 + \sqrt{5})^{n+1} - (1 - \sqrt{5})^{n+1}] \,. \qquad (1a)$$

Let ni(x) denote the integer nearest to x, i.e. $|x - ni(x)| < 0.5$. Then Eq. (1a) can be written also as

$$Z(P_n) = ni[20^{-1/2}\, 2^{-n}\, (1 + \sqrt{5})^{n+1}] \,. \qquad (1b)$$

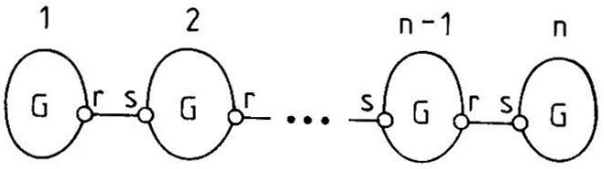
In the above formulas P_n symbolizes the molecular graph of the normal alkane, i.e. the path with n vertices:



P_n

The discovery of Eq. (1) was followed by a rather limited number of other combinatorial formulas [10-12].

In the present paper we calculate the Hosoya index of a general class of polymers whose molecular graph X_n has the following structure:



X_n

In the above diagram the monomer unit is represented by a graph G. The n monomer units in X_n are coupled to each other via the atoms r and s.

The formula for $Z(X_n)$ generalizes quite a few previously known results, not only in the theory of the Hosoya index, but also in the enumeration of Kekulé structures and elsewhere.

RECURRENCE RELATION FOR $Z(X_n)$

If G is an arbitrary molecular graph whose (arbitrary) edge e connects the vertices u and v, then the Hosoya index of G satisfies the identity [1]:

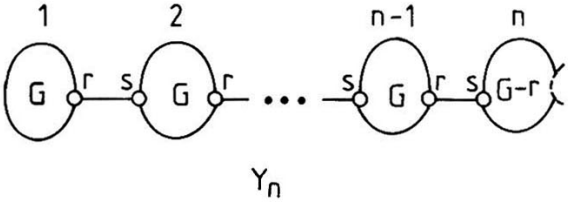
$$Z(G) = Z(G-e) + Z(G-u-v) \qquad (2)$$

where G-e is the graph obtained by deletion of e from G, and G-u-v is the graph obtained by deletion of the vertices u and v from G. Another relation needed in the calculation of Z is [1]:

$$Z(G_1 \cup G_2) = Z(G_1) \cdot Z(G_2) \qquad (3)$$

where $G_1 \cup G_2$ denotes the graph composed of two disconnected components G_1 and G_2.

Using (2) and (3) we can deduce a recurrence relation for $Z(X_n)$. In order to do this, we introduce an auxiliary system Y_n:



As indicated on the above diagram, Y_n is obtained from X_n by deleting the vertex r from the n-th monomer unit.

Applying (2) and (3) to the edge connecting the (n-1)-th and the n-th monomer units of X_n we immediately arrive at

$$Z(X_n) = Z(G)\ Z(X_{n-1}) + Z(G-s)\ Z(Y_{n-1}) \ . \qquad (4)$$

In a fully analogous manner we conclude

$$Z(Y_n) = Z(G-r)\ Z(X_{n-1}) + Z(G-r-s)\ Z(Y_{n-1}) \ . \qquad (5)$$

Expressing $Z(Y_{n-1})$ from (4) and substituting it back into (5) one finally obtains

$$Z(X_n) = [Z(G) + Z(G-r-s)]Z(X_{n-1})$$
$$+ [Z(G-r)\ Z(G-s) - Z(G)\ Z(G-r-s)]Z(X_{n-2}) \ . \qquad (6)$$

Together with the initial conditions

$$Z(X_0) = 1 \quad ; \quad Z(X_1) = Z(G) \qquad (7)$$

Eq. (6) enalbles one to calculate recursively $Z(X_n)$ for all values of $n > 1$.

COMBINATORIAL FORMULA FOR $Z(X_n)$ AND SOME OF ITS PROPERTIES

Bearing in mind that (6) is a second order linear recurrence relation and using standard mathematical techniques [13] we have

$$Z(X_n) = a_1 (t_1)^n + a_2 (t_2)^n$$

where t_1 and t_2 are the roots of the equation

$$t^2 = [Z(G) + Z(G-r-s)]t + [Z(G-r) Z(G-s) - Z(G) Z(G-r-s)] .$$

The multipliers a_1 and a_2 are independent of n, and are determined by the initial conditions (7). Direct calculation gives

$$Z(X_n) = (2^{n+1} R)^{-1} [(Q^- + R)(Q^+ + R)^n - (Q^- - R)(Q^+ - R)^n] \qquad (8)$$

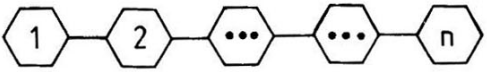
where

$$Q^+ = Z(G) + Z(G-r-s) \qquad (8a)$$

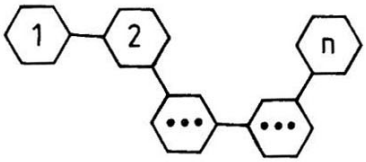
$$Q^- = Z(G) - Z(G-r-s) \qquad (8b)$$

$$R = [(Q^-)^2 + 4 Z(G-r) Z(G-s)]^{1/2} . \qquad (8c)$$

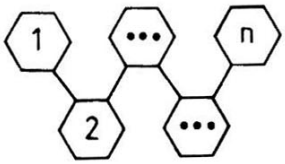
As examples we present the expressions for the Hosoya index of para-, meta- and ortho-polyphenylenes, I, II and III, respectively.



I



II



III

$$Z(I) = 452^{-1/2}[(\sqrt{113} + 7)(11 + \sqrt{113})^n + (\sqrt{113} - 7)(11 - \sqrt{113})^n] =$$

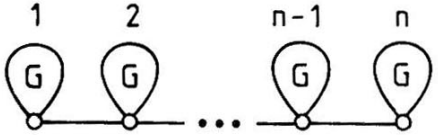
$$= ni[452^{-1/2}\ (\sqrt{113} + 7)(11 + \sqrt{113})^n]$$

$$Z(II) = 1924^{-1/2}\ 2^{-n}[(\sqrt{481} + 15)(21 + \sqrt{481})^n + (\sqrt{481} - 15)(21 - \sqrt{481})^n] =$$

$$= ni[1924^{-1/2}\ 2^{-n}\ (\sqrt{481} + 15)(21 + \sqrt{481})^n]$$

$$Z(III) = 1700^{-1/2}\ 2^{-n}[(\sqrt{425} + 13)(23 + \sqrt{425})^n + (\sqrt{425} - 13)(23 - \sqrt{425})^n]\ .$$

The special case of X_n when r = s is worth particular attention. It corresponds to the system depicted below:



The special case of Eq. (8) for r = s is obtained by setting $Z(G-r-s) = 0$. Hence, if r = s,

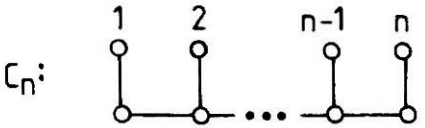
$$Z(X_n) = (2^{n+1}\ R)^{-1}[[Z(G) + R]^{n+1} - [Z(G) - R]^{n+1}] \qquad (9)$$

where

$$R = [Z(G)^2 + 4\ Z(G-r)^2]^{1/2} .$$

As an example consider P_n. Then G is the one-vertex graph, $Z(G) = 1$ and $Z(G-r) = 1$. Hence Eq. (9) reduces to Eq. (1).

Another special case of Eq. (9), namely for the "comb" C_n:



where $Z(G) = 2$, $Z(G-r) = 1$, was previously reported [6]:

$$Z(C_n) = 8^{-1/2}[(1 + \sqrt{2})^{n+1} - (1 - \sqrt{2})^{n+1}] =$$

$$= ni[8^{-1/2}\ (1 + \sqrt{2})^{n+1}] . \qquad (10)$$

Formula (8) solves also the problem of the behaviour of the Hosoya index of very long (or more precisely: of infinitely long) polymer chains. It is evident that $Z(X_n)$ increases exponentially with n. Furthermore,

$$\lim_{n\to\infty}\ n^{-1}\ \log Z(X_n) = \log[(Q^+ + R)/2] .$$

CONNECTION WITH THE NUMBER OF KEKULÉ STRUCTURES

It is known [14] that the number of Kekulé structures obeys the following relations:

$$K(G) = K(G-e) + K(G-u-v) \tag{11}$$

$$K(G_1 \cup G_2) = K(G_1) \cdot K(G_2) \tag{12}$$

where the notation is the same as in Eqs. (2) and (3). One should observe the complete analogy between Eqs. (11) & (12) and Eqs. (2) & (3), respectively. As a consequence of this, whatever result is obtained for Z using (2) and (3), an analogous result will exist for K. In particular,

$$K(X_n) = (2^{n+1}\,\tilde{R})^{-1}\,[(\tilde{Q}^- + \tilde{R})(\tilde{Q}^+ + \tilde{R})^n - (\tilde{Q}^- - \tilde{R})(\tilde{Q}^+ - \tilde{R})^n] \tag{13}$$

where

$$\tilde{Q}^+ = K(G) + K(G-r-s)$$

$$\tilde{Q}^- = K(G) - K(G-r-s)$$

$$\tilde{R} = [(\tilde{Q}^-)^2 + 4\,K(G-r)\,K(G-s)]^{1/2} .$$

Eq. (13) can be significantly simplified.

(a) If the monomer unit G has even number of atoms, then K(G-r) and K(G-s) must be equal to zero. Consequently, $\tilde{R} = \tilde{Q}^-$ and

Eq. (13) reduces to the well-known formula

$$K(X_n) = K(G)^n \ .$$

(b) If the monomer unit G has odd number of atoms, then K(G) and also K(G-r-s) are necessarily equal to zero. Then $\tilde{Q}^+ = \tilde{Q}^- = 0$ and Eq. (13) reduces to

$$K(X_n) = 0 \qquad \text{if } n = 1,3,5,\ldots$$

$$K(X_n) = [K(G-r)\ K(G-s)]^{n/2} \qquad \text{if } n = 2,4,6,\ldots$$

SOME FURTHER CONNECTIONS

The matching polynomial [15,16] obeys the relations

$$\alpha(G) = \alpha(G-e) - \alpha(G-u-v)$$

$$\alpha(G_1 \cup G_2) = \alpha(G_1)\cdot\alpha(G_2) \ .$$

Therefore, if one writes $\alpha(G)$, $\alpha(G-r)$, $\alpha(G-s)$ and $-\alpha(G-r-s)$ instead of Z(G), Z(G-r), Z(G-s) and Z(G-r-s), respectively, in Eqs. (8a-8c), then the right-hand side of (8) will just reproduce the matching polynomial of X_n.

Similarly, if e is a bridge (i.e. an edge which does not belong to any cycle), then the following relation is satisfied by the characteristic polynomial of the graph G [17]:

$$\phi(G) = \phi(G-e) - \phi(G-u-v) \ .$$

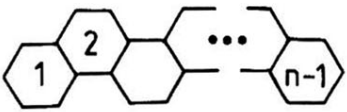
Since in addition [17]

$$\phi(G_1 \cup G_2) = \phi(G_1)\cdot\phi(G_2)$$

the right-hand side of (8) will be equal to $\phi(X_n)$ if in (8a-8c) $Z(G)$, $Z(G-r)$, $Z(G-s)$ and $Z(G-r-s)$ are replaced by $\phi(G)$, $\phi(G-r)$, $\phi(G-s)$ and $-\phi(G-r-s)$, respectively.

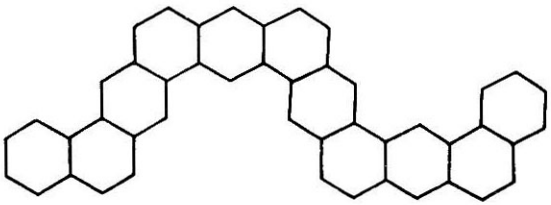
It has been demonstrated [18] that every unbranched catacondensed benzenoid hydrocarbon B can be associated with a tree T(B), such that the number of Kekulé structures of B is equal to the Hosoya index of T(B) [19]. In some cases the tree T(B) belongs to the class X_n and then formula (8) is also the combinatorial expression for the number of Kekulé structures of B.

For example, P_n is the tree associated with the zig-zag polyacene with n-1 hexagons:



Whence, Eq. (1) reproduces also the number of Kekulé structures of the above benzenoid molecule. This is a long-known result [14].

As another result of this kind note that the comb C_n is associated with the catacondensed benzenoid molecule whose structure is illustrated for n = 6:



Then the number of Kekulé structures of these benzenoid hydrocarbons is reproduced by the formula (10). Using a completely different way of reasoning, the same result (in a somewhat more generalized version) was obtained in a recent paper [20] (see also Eq. (6.18) in Ref. [14]).

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